High-Pressure Measurements of Hydrogen Phase IV Using Synchrotron Infrared Spectroscopy

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Phase IV of dense solid hydrogen has been identified by its infrared spectrum using high-pressure synchrotron radiation techniques. The spectrum exhibits a sharp vibron band at higher frequency and lower intensity than that for phase III, indicating the stability of molecular H_2 with decreased intermolecular interactions and charge transfer between molecules. A low-frequency vibron having a strong negative pressure shift indicative of strongly interacting molecules is also observed. The character of the spectrum is consistent with an anisotropic, mixed layer structure related to those recently predicted theoretically. Phase IV was found to be stable from 220 GPa (300 K) to at least 340 GPa (near 200 K), with the I-III-IV triple point located. Infrared transmission observed to the lowest photon energies measured places constraints on the electronic properties of the phase.

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The behavior of element one at high pressure is a subject of continuing interest because it is fundamental to understanding the nature of condensed matter, and its intriguing if not unique properties predicted at very high density. Early work established the molecular phases I, II, and III and the persistence of paired states of hydrogen to megabar pressures (>100 GPa) and lower temperatures [1] in the search for predicted novel quantum states in the material at very high compressions [2]. Numerous structures have been predicted for these dense molecular phases [3–11], including those that involve closure of the band gap at multimegabar pressures (e.g., 300 GPa), which corresponds to greater than 12-fold compression of the zero-pressure solid ($\rho/\rho_0 > 12$ relative densities). Identifying the exact structures, electronic properties, and stability fields of these solid molecular phases over a broad range of temperatures is essential for confirming and understanding the high-density solid and fluid phases forms (see Ref. [12]).

Despite the well-known experimental difficulties, recent advances in static compression techniques have allowed the study of hydrogen at multimegabar pressures not only at low but also elevated temperatures, leading to new findings [13–15]. Eremets and Troyan [13] reported a pressure-induced onset in electrical conductivity at 260 GPa and room temperature, together with Raman and optical spectra, and identified that transition as metallization. Howie *et al.* [14] reported a transition to phase IV and proposed a phase boundary over a limited range. Zha *et al.* [15] carried out a broad survey of the stability of the molecular phases of hydrogen, focusing on temperatures from 10 K to 200 K. A broad stability range for phase III was confirmed, and no evidence for metallization was established based on infrared (IR) absorption measurements to 360 GPa, in contrast to earlier claims. Moreover, it has been reported that hydrogen transforms to another phase well below 300 GPa (phase V) based on additional experiments, including analyses of published data [11,16]. New experiments are required to clarify these issues.

These recent experimental results have stimulated new but conflicting theoretical work on the behavior of hydrogen in this *P*-*T* regime [4,5,7–11]. Azadi and Khune [7] find a broad stability field for phase III, in agreement with recent measurements [15] and that a $P6_3/m$ structure is the most stable phase, in contrast to the earlier proposal that phase III has the $C2/c$ structure [4,5]. This phase is predicted to remain nonmetallic to >400 GPa. Pickard *et al.* [11] find the *Pc* and *Cc* structures to be stable at high temperature above 260 GPa and obtain a phase boundary similar to that reported for the transition found by Howie *et al.* [14], although the *Cmca*-4 structure was subsequently found to be more stable above 260 GPa [11]. They also predicted, in contrast to other results, that phase III transforms to the *Cmca*-12 structure near 280 GPa, later corrected to 240 GPa at 300 K with no stability field for the *Pc* structure [11]. This scheme was pointed out by Liu *et al.* [9], whose calculations supported the claimed metallization at 270 GPa. Meanwhile, *GW*-corrected band structure calculations by Lebegue *et al.* [8] predicted gap closure in *Cmca*-12 at that pressure, although those calculations find the $C2/c$ and *Pbcn* structures to have lower enthalpies at that pressure. They identified the new phase to be *Cmca*-12 based on agreement with the pressure of the predicted gap closure and the transition pressure identified as metallization in Ref. [13], in which the new phase at 270 GPa was also identified as *Cmca*-12. Very recent calculations predict distortions of the *Pc* structure and provide estimates of band gap closure in the *Cmca*-4 phase [10].

Spectroscopic techniques are key probes for identification and characterization of the phases of hydrogen at multimegabar pressures. IR spectroscopy, in particular, has been essential, as measurements of the frequency and distribution of vibrational excitations are distinct signatures of bonding, intermolecular interactions, phase transitions, and crystal structures [17,18]. IR spectroscopy is a crucial tool for testing theoretical predictions of candidate structures (e.g., Refs. [4,11]). Moreover, measurements of the optical conductivity in the IR range are required to identify electronic transitions such as insulator-metal transitions. Because the indirect gap must close prior to the direct gap if the molecules are intact, measurements of the direct gap (e.g., visible light) are insufficient for identifying the onset of band gap closure. Here we report IR spectra over a broad range of *P*-*T* conditions in order to examine transitions proposed based on both theory and experiment. The results provide important constraints on the structure of phase IV and show that it is similar to several of the structures predicted theoretically. The measurements reveal no free carrier absorption characteristic of the metallic phases proposed previously but instead is that of a semiconductor or semimetal over the *P*-*T* range investigated.

Experiments were carried out using an extension of techniques described previously [15]. Briefly, we used diamond anvil cells to cycle both temperature and pressure to provide careful isothermal and isobaric adjustments, and it was possible to reach temperatures above 300 K. Infrared spectra were measured at beam line U2A at the National Synchrotron Light Source, Brookhaven National Laboratory. The samples were exposed to minimal laser excitation in order to prevent damage to the anvils and loss of sample. Pressures were determined from the diamond Raman edge and previously established shifts in the vibron [15,19–21]. Further details are provided in Ref. [22].

Selected spectra in the region of the vibron are shown in Fig. 1. On heating the sample at 268 GPa, the strong vibron of phase III disappears and new vibron bands appear. One of the new vibron bands appears at a significantly higher frequency (4435 cm^{-1} versus 4180 cm^{-1} for phase III at the same pressure) with approximately one-tenth the integrated intensity. Its appearance is sharp and fully reversible, indicating the formation of a new phase. In addition, a low-frequency vibron band appears at 3950 cm^{-1}; in contrast to the higher vibron, its frequency decreases strongly with pressure. Measurements carried out during isothermal compression at 300 K show a splitting of the principal vibron and strong softening of lower vibron that is fully consistent with the isobaric measurements.

We attribute these spectral changes to the transition from phase III to phase IV. The difference between the vibron spectra of the two phases is striking. The *P*-*T* dependencies of the vibron frequencies across the transition are shown in Fig. 2. The high frequency vibron in phase IV is remarkably independent of both pressure and temperature over the range of conditions measured. A high frequency vibron is also reported in the Raman spectrum of this phase [14], which has a weak pressure dependence and is shifted relative to the IR mode. The IR bands are assigned to the coupled antisymmetric stretching mode (ν_a) for the two different types of molecules in the structure (Fig. 2). These complement the symmetric stretching mode observed by Raman scattering (ν_s) [14]. This shift can be used to infer

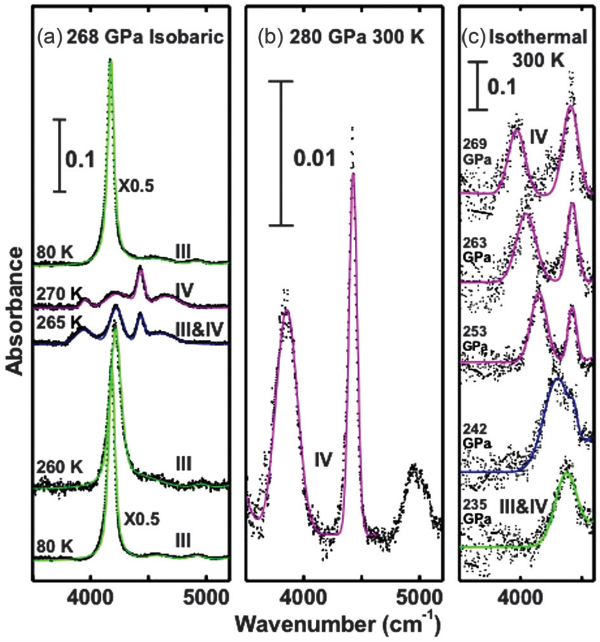

FIG. 1 (color). Selected synchrotron IR spectra at different temperatures in the vicinity of the vibrons (intramolecular stretching mode). (a) Isobaric measurements at 268 GPa through the III-IV phase transition. (b) Detail in the vibron region at 280 GPa and 295 K. The spectrum was baseline corrected after treatment to remove interference fringes. Residual diamond absorption also contributes to the feature at 3950 cm^{-1} at this pressure, so the frequency of the hydrogen peak carries some uncertainty. (c) Isothermal compression showing the evolution of the spectrum through phases III and IV at 300 K. The fitted lines show the peaks attributed to each phase (see Refs. [15,22] for further details). The bar gives the absorbance scale for each panel.

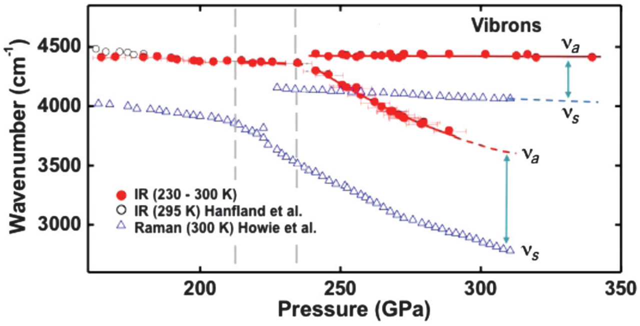

FIG. 2 (color). Pressure dependence of the frequencies of the principal hydrogen vibrons through phases I, III, and IV at 230–300 K. Earlier IR vibron data for phase I [17] and recent Raman results for phase IV [14] are indicated. The two pairs of symmetric (ν_s) and antisymmetric (ν_a) coupled vibron excitations observed by Raman and IR, respectively, are indicated.

an intermolecular coupling with $\Delta\nu_{a\text{-}s} = 300\ \mathrm{cm}^{-1}$ increasing at a rate of $1\ \mathrm{cm}^{-1}/\mathrm{GPa}$. The lower frequency vibrons observed in both the IR and Raman spectra exhibit strong softening, indicating weakened intramolecular bonding and enhanced intermolecular interactions, with $\Delta\nu_{a\text{-}s} = 830\ \mathrm{cm}^{-1}$. This splitting is significantly larger than in other hydrogen phases [1] and is remarkably pressure independent (for example, $\Delta\nu_{a\text{-}s}$ increases from $3\ \mathrm{cm}^{-1}$ to $510\ \mathrm{cm}^{-1}$ at 180 GPa in phase I [17]). Quantitative predictions of these effects will be an important challenge to theory (e.g., Ref. [23]).

The extended *P-T* range of our measurements provides a determination of the III-IV phase boundary (Fig. 3). The pressure of the electrical conductivity onset reported by Eremets and Troyan [13] is close to the proposed phase boundary observed in the current study, so we attribute their reported transition to the III-IV transition. These results largely agree with changes observed by Raman scattering and confirm the assignment of the transition to phase VI at the *P-T* conditions where the data overlap. Apparent discrepancies are likely due to different calibrations and reflect uncertainties in the pressure scale employing the diamond Raman edge (see Ref. [15]). Data from the current IR experiments extend the phase boundary to both higher temperature and higher pressure. The measurements indicate that phase IV is stable to at least 340 GPa and temperatures of 200 K. Spectra collected above room temperature constrain the I-III-IV triple point to be at 335 (±15) K and 225 (±10) GPa on the pressure scale used.

The character of the spectra provides key constraints on the structure of phase IV. In this regard, we note that the spectrum of phase IV differs significantly from that of phases I, II, and III. The modes for phase IV separate into two groups in both the IR and Raman spectra [22], indicating two different types of chemical bonding. The high-frequency Raman mode of phase IV is close to the IR vibron of phase III [13–15,19], which appears at the top of the vibron band for the hcp structure of phase I [1]. This high-frequency vibron is both at a much higher frequency, and significantly weaker than that of phase III, which indicates much weaker intermolecular interactions at higher temperatures. Temperature therefore plays an important role in weakening the intermolecular coupling of these molecules in the structure. Taken together with the previously reported spectra [13,14], the results show that phase IV exhibits fluidlike properties associated with strong quantum effects and anharmonicity [24].

Our measurements reveal transmission in the IR down to $600\ \mathrm{cm}^{-1}$ over the entire *P-T* range studied (Fig. 4), and the absence of a free-carrier absorption characteristic of a good metal. As for phase III [15], Drude model fits of the lowest energy portions of the spectra, assuming closure of the band gap, indicate that the plasma frequency energy $\hbar\omega_p$ must be less than 0.2 eV at the highest pressures, in contrast to $\hbar\omega_p$ of several eV for a good metal. No temperature dependence of broad features associated with a possible Drude edge was observed for phase IV. The magnitude of the conductivity onset reported in Ref. [13] is consistent with a semiconductor to semimetal transition, although other interpretations are possible (see Ref. [15]). The transition is sharp and completely reversible (like other transitions studied to date in hydrogen, e.g., involving I, II, III, melt), in contrast to the hysteresis in the previously reported transition [13,25]. The IR spectrum calculated by Pickard *et al.* [11] for a structure with *Pc* symmetry at these pressures contains a single vibron band with a frequency and intensity (relative to that calculated

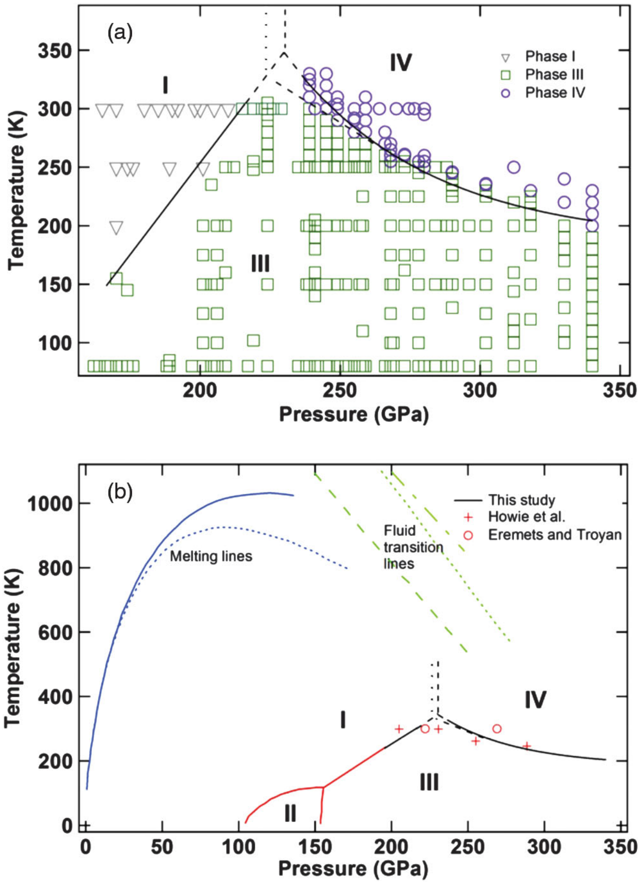

FIG. 3 (color). Phase diagram of hydrogen to multimegabar pressures. (a) *P-T* points measured in phases I, III, and IV. The phase assignment for each *P-T* point is identified from IR-absorption measurements during isobaric temperature cycling or isothermal compression (e.g., Figs. 1 and 2). The estimated I-III-IV triple point is indicated. The uncertainty in the value arises from the degree of curvature assumed in the III-IV line as the triple point is approached. (b) Phase diagram of hydrogen over a broader *P-T* range. Previous determinations of the changes observed by Raman and conductivity are indicated [13,14]; additional data have been reported recently in Ref. [28]. The melting lines are from Refs. [29,30] (and references therein). The fluid transition lines correspond to the predicted fluid-fluid and plasma phase transitions [30].

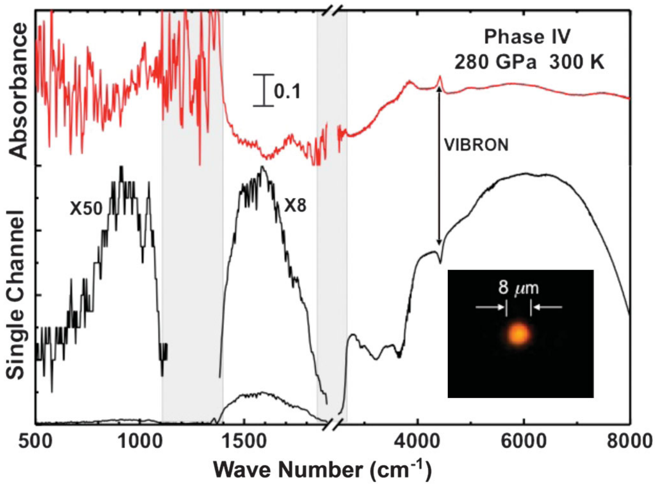

FIG. 4 (color). IR absorption and single channel spectra of hydrogen in phase IV at 280 GPa and room temperature. The upper trace is the absorption spectrum, and the lower spectrum is the synchrotron radiation signal transmitted through the sample, uncorrected for long-wavelength diffraction effects and detector sensitivity. Light gray boxes cover the opaque regions of the diamond anvils due to nitrogen impurity absorption (1100–1400 cm^{-1}) and multiphonon absorption at 1850–2500 cm^{-1}. The measurements demonstrate that hydrogen at these conditions is transparent down to at least 600 cm^{-1}. Analysis indicates an upper bound on the absorption coefficient σ of 10^3 cm^{-1} at the lowest energy. The strongest vibron is indicated in the two traces. Inset: Transmitted light photomicrograph of the 6–8 μm diameter sample surrounded by the opaque gasket, showing optical transmission of the hydrogen at these conditions. The yellow color arises from visible absorption from the hydrogen as well as residual absorption by the diamond anvils (as for measurements on phase III [15]).

for phase III as assigned to $C2/c$), in fair agreement with experiment. On the other hand, additional vibron excitations not predicted theoretically are measured experimentally, indicating that the structure is more complex. In addition, changes in the spectra at the highest temperatures and the curvature in the III-IV line suggest transitions to structurally related phases. However, the results rule out major structural and electronic transitions, such as that to the *Cmca*-12 proposed at the *P*-*T* conditions studied here [11,16] (see also Ref. [22]).

In conclusion, IR spectra of hydrogen measured over a broad *P*-*T* range reveal that phase IV exhibits both very strong and weak interactions between molecules and optical transparency extending to low photon energies. The very different vibron frequencies, intensities, and splittings indicate that phase IV has a distinct dynamical structure compared to hydrogen phases previously documented experimentally. Aspects of the vibrational spectrum agree with that predicted for layered structures obtained in recent calculations, but additional excitations are observed experimentally indicating the existence of a more complex structure (or structures). The spectral signature of the strongly interacting hydrogen molecules is consistent with the presence of graphenelike sheets, a configuration predicted in early calculations on dense hydrogen [26]. The existence of such sheets has implications for the electronic properties of dense hydrogen. These results thus place important constraints on the growing number of theoretical studies underway on this fundamental system (e.g., Refs. [10,27]).

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